

The Copper-rich Alloys of the Copper-nickel-tin System¹

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*Based on a Dissertation Submitted in Partial
Fulfillment of the Requirements for the Degree
of Doctor of Philosophy at the University of
Michigan.*

*Preprint, American Institute of Mining
and Metallurgical Engineers, Institute of
Metals Division.*

(Buffalo Meeting, October, 1932)

Ann Arbor
1932

*27699



The Copper-rich Alloys of the Copper-nickel-tin System*

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DURING recent years nickel has had an increasingly important role as an alloying element in the copper-tin bronzes. Nickel additions not only produce better casting alloys but also make alloys whose properties can be varied by precipitation hardening; thus leading to increased commercial application of copper-nickel-tin alloys.

Recent investigations have indicated a decrease in the solubility of tin in the alpha phase as the annealing temperature is lowered and as the nickel content is increased within certain limits. A further change caused by the nickel additions is produced in the excess phase of the copper-tin bronzes. The alpha plus delta eutectoid is replaced by a clear precipitated constituent in the alloys containing up to 15 per cent tin and not less than 1 per cent nickel.

This paper has a dual purpose. The first is to present a new determination of the alpha-phase boundary in alloys containing from 0 to 20 per cent nickel, together with the liquidus and solidus temperatures above that field. The second purpose is to give the equilibrium conditions existing in alloys exceeding the alpha phase containing up to 31 per cent tin and 5 per cent nickel, so that the disappearance of the alpha plus delta eutectoid constituent may be explained.

After considering the earlier investigations of the related alloy systems and the experimental procedure used in this investigation, the alloys will be discussed in groups as separate quasibinary systems containing constant amounts of nickel. The systems considered contain 0, 1, 2, 3, 5, 10 and 20 per cent nickel. The straight copper-tin system was reinvestigated in order to establish a foundation on which to build the remaining material. The 1 per cent nickel alloys studied give the relations existing in the region of the eutectoid transformation between the copper-tin system and the 2 per cent nickel copper-tin system which has been investigated in detail. The thorough examination of the latter system was made since 2 per cent of nickel is representative of the commercial additions to the cast bronzes and also because it is sufficient to produce

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decided changes in the copper-tin system. The 3 and 5 per cent nickel systems show the effect of increasing amounts of nickel on the equilibrium conditions. Only the alpha-phase boundary was determined for the 10 and 20 per cent nickel copper-tin systems.

REVIEW OF LITERATURE

The results of investigations of the copper-nickel, copper-tin, nickel-tin and copper-nickel-tin systems should be considered before considering the ternary system, because of the close relationships between the phases existing in the ternary system and those of the three binary systems.

The Binary Systems

Copper-nickel System.—Guertler and Tammann¹ published a diagram of this system in 1907. Copper and nickel form a complete series of solid solutions, as the metals are entirely miscible in one another in the solid state. The magnetic transformation, which is not accompanied by a structural change, is depressed by the addition of copper to room temperature at about 40 per cent of copper.

Copper-tin System.—The copper-tin system has been studied by many investigators because of its complicated phase transformations and the wide range of industrial applications of these alloys. Although the equilibrium conditions of this system have been the subject of a great amount of research, the equilibrium diagram is still in doubt. The main points pertinent to the present investigation in which the various diagrams disagree are (1) the solubility of tin in the alpha phase, (2) the nature of the horizontal at 590° C. and the beta inversion, (3) the formation of the alpha + delta eutectoid, (4) the composition of the delta phase. Bearing these points in mind, the results of the most important investigations of the copper-tin system are summarized in Table 1.

Nickel-tin System.—The nickel-tin system has not been the object of much investigation. In 1907 Guillet² developed a diagram showing an alpha solubility of 5 per cent tin. The entire system was made up of various solid solutions with a eutectic, at 64 per cent nickel, formed between the alpha and beta solid solutions.

A year later Voss³ found that the alpha phase extended to 15 per cent tin. Unlike the previous work, the remaining phases consisted of a series of compounds of nickel and tin instead of solid solutions. A eutectic containing Ni₃Sn and alpha was formed at 69 per cent nickel. Both investigations showed a constant composition for the alpha boundary from the eutectic temperature to room temperature.

¹ Guertler and Tammann: *Ztsch. f. anorg. Chem.* (1907) **52**, 25.

² Guillet: *Rev. de Mét.* (1907) 535.

³ Voss: *Ztsch. f. anorg. Chem.* (1908) **57**, 38.

TABLE 1.—*Investigations of the Copper-tin System*

Investigator	Date	Solubility of Tin in Alpha Phase, Per Cent		Nature of Change at 590° C.	Eutectoid of Alpha + Delta Formed from	Composition of Delta Phase
		At Melt- ing Point	At Room Temp.			
Heycock and Neville ^a	1903	9	9		Beta	Cu ₃ Sn
Shepherd and Blough ^b	1906	10	13		Beta	Solid solution (25–33 % tin)
Hoyt ^c	1913	9	10	Beta to alpha + gamma	Gamma	Solid solution (27–32 % tin)
Bauer and Vollenbruck ^d	1922	13.9	13.9	Beta to alpha + gamma	Gamma	Cu ₃ Sn
Isihara ^e	1924	10	11	Change in alpha	Beta	Cu ₃ Sn
Stockdale ^f	1925	13.3	16	Polymorphic		
Westgren and Phragmen ^g	1926					Solid solution over very small range. Cu ₃₁ Sn ₅ is solvent. $a = 17.91\text{Å}$
Hansen ^h	1927	16 (518° C.)	14			
Raper ⁱ	1927			Polymorphic Change in the beta	Beta	Compound
Matsuda ^j	1928	15	15	Beta to alpha + gamma	Beta	Cu ₃ Sn
Carson ^k	1929	13 (16 %, 520° C.)	15		Beta	Solid solution (32–33 % tin)

References:

- ^a Heycock and Neville: *Phil. Trans. Roy. Soc.* (1903) **202**, 1.
^b Shepherd and Blough: *Jnl. Phys. Chem.* (1906) **10**, 630.
^c Hoyt: *Jnl. Inst. Metals* (1913) **10**, 259.
^d Bauer and Vollenbruck: *Ztsch. f. Metallkunde* (1923) **15**, 119–125, 191–195.
^e Isihara: *Jnl. Inst. Metals* (1924) **31**, 315.
^f Stockdale: *Jnl. Inst. Metals* (1925) **34**, 111.
^g Westgren and Phragmen: *Ztsch. f. Metallkunde* (1926) **18**, 279–284.
^h Hansen: *Ztsch. f. Metallkunde* (1927) **19**, 407.
ⁱ Raper: *Jnl. Inst. Metals* (1927) **38**, 217.
^j Matsuda: *Sci. Repts. Tohoku Imp. Univ.* (1928) **17**, 144.
^k Carson: *Canadian Min. & Met. Bull.* (Jan., 1929).

The Ternary System

Copper-nickel-tin System.—In 1928 Price, Grant and Phillips⁴ published a diagram giving the 800° C. isotherm of the alpha-phase boundary. The solubility gradually decreased from 13 per cent tin and 0 per cent nickel to a minimum at about 8 per cent tin and 19 per cent nickel, and then increased to 15 per cent tin and 0 per cent copper on the high-nickel side of the diagram. The excess phase was considered to be beta in all cases.

In the discussion of that paper, Wise gave the alpha boundary at 800°, 700° and 300° C. for alloy compositions which range from 0 per cent

⁴ Price, Grant and Phillips: *Trans. A.I.M.E.* (1928) **78**, Inst. Metals Div., 503.

nickel to approximately 40 per cent nickel. The 800° C. isotherm is practically the same as that given by Price, Grant and Phillips. At 700° C. the solubility is about 3 per cent less than at 800° C. At 300° C. the solubility decreased abruptly from 13.5 per cent tin and 0 per cent nickel to a minimum at about 2.5 per cent tin and 5 per cent nickel, followed by a gradual increase to 7 per cent tin and 40 per cent nickel. Wise found that, owing to the decrease in solubility between high and low temperatures, it was possible to age-harden alloys having compositions within this range.

In 1930 Upthegrove, Wilson and Rhines⁵ published their results on the effect of small percentages of nickel on the hardness and microstructure of an 85 per cent copper and 15 per cent tin base alloy. The nickel was substituted for the copper, leaving the percentage tin constant. The addition of very small amounts of nickel did not produce any effect on the microstructure except to increase the percentage of eutectoid. With 1 per cent nickel two changes occurred. The alpha of the eutectoid disappeared and a dispersed constituent was found in the alpha. With increasing nickel content up to 10 per cent there was an increase in the amount and size of the dispersed phase.

In 1931 Pilling and Kihlgren⁶ published the results of an investigation concerning the effects of nickel on the properties of a number of bronze foundry alloys.

EXPERIMENTAL PROCEDURE

Melting and Heat Treatment of the Alloys

The metals used in this study were electrolytic copper (99.96 per cent copper), Baker's C.P. tin and electrolytic nickel which was obtained from the International Nickel Co. The alloys used for the tests were melted in a Hoskins carbon resistor furnace. In the making of the melts of the copper-nickel-tin alloys an atmosphere of hydrogen was maintained at all times over the surface of the metal; 500-gram melts were used for the alloys. The fact was recognized that this type of alloy has a tendency towards inverse segregation, so great care was taken in melting and casting the alloys.

Table 2 gives the computed compositions of the alloys that were prepared. A sufficient number of alloys in each quasibinary system were analyzed to show that there was a very close agreement between the computed and analytical compositions of the alloys.

In order to anneal a large number of specimens at one time and to obtain a uniform temperature throughout a reasonable furnace length, an electric muffle furnace containing a copper block was used, patterned after the annealing furnace used by Dix and Richardson.⁷ The furnace

⁵ Upthegrove, Wilson and Rhines: *Proc. Amer. Soc. Test. Mat.* (1930) **30**, 512-519.

⁶ Pilling and Kihlgren: *Trans. Amer. Foundrymen's Assn.* (1931) **2**, 93-110.

⁷ Dix and Richardson: *Trans. A.I.M.E.* (1926) **73**, 560-580.

TABLE 2.—*Computed Compositions of the Alloys*
Weight Per Cent

Nickel	Tin	Copper	Nickel	Tin	Copper	Nickel	Tin	Copper
0	14.5	85.5	3	1	96	10	7	83
0	15.5	84.5	3	1.5	95.5	10	8	82
0	16	84	3	2	95	10	9	81
0	17	83	3	3	94	10	10	80
0	27	73	3	4	93	10	15	75
0	31.8	68.2	3	5	92	10	18	72
			3	6	91			
1	27	72	3	9	88	20	2	78
1	28	71	3	10	87	20	3	77
1	29	70	3	11	86	20	4	76
1	30	69	3	11.55	85.45	20	5	75
			3	12.5	84.5	20	6	74
2	1	97	3	13.5	83.5	20	7	73
2	2	96	3	14.5	82.5	20	8	72
2	3	95	3	18	79	20	9	71
2	3.5	94.5	3	22	75	20	15	65
2	4	94	3	26	71	20	18	62
2	5	93	3	29	68			
2	6	92						
2	7	91	5	1	94			
2	8	90	5	1.5	93.5			
2	9	89	5	2	93			
2	10	88	5	3	92			
2	11	87	5	4	91			
2	11.5	86.5	5	7	88			
2	12	86	5	8	87			
2	12.5	85.5	5	9	86			
2	13	85	5	10	85			
2	13.5	84.5	5	11	84			
2	14.2	83.8	5	12	83			
2	15	83	5	13	82			
2	16	82	5	15	80			
2	18	80	5	18	77			
2	20	78	5	22	73			
2	22	76	5	26	69			
2	23	75	5	29	66			
2	24	74						
2	25	73	10	1	89			
2	26	72	10	1.5	88.5			
2	27	71	10	2	88			
2	29	69	10	3	87			
2	31	67	10	4	86			
			10	5	85			
			10	6	84			

temperature was controlled by an automatic controller and was held to $\pm 2^\circ \text{C.}$ during the annealing period.

No doubt one of the factors contributing to the wide variation in the position of the alpha-phase boundary and the location of other phase fields of the copper-tin system, as reported by previous investigators, was the length of time the alloys were annealed. The heating time used by various investigators has varied all the way from 45 minutes to 120 hours.

In the determination of the alpha-phase boundary in the present research, limiting points were found for temperatures of 780° , 700° , 500° , 300°C. and room temperature for each constant nickel percentage excepting the 1 per cent series. Sets of five or six samples of varying composition within which the boundary was expected to be found were placed in separate tubes in the copper block. All of them were initially annealed at 780°C. for 120 hr. At the end of that time the tube containing the alloys to be quenched at 780°C. was removed and quickly immersed in ice water. The furnace was then allowed to cool slowly to 700°C. , where it was maintained for 24 hr. The tube containing the samples to be quenched at 700°C. was removed and quenched. The furnace was cooled to 500°C. and then to 300°C. , where the same annealing time and quenching procedure was conducted in each case. A fifth set of samples was slowly cooled to room temperature. This method required approximately 130 hr. for the furnace to cool from 780°C. to room temperature, or a total time of 250 heating hours for the last set of samples.

In studying the phase changes occurring in alloys of high tin content a lower initial annealing temperature, 725°C. , was used on account of the lower melting points of the alloys.

Thermal Analysis

The method of determining the melting points of the alloys is for the most part the same as described by Wood and Cork.⁸ The samples, weighing approximately 175 grams, were cooled and heated at the rate of 3 to 5°C. per minute.

Thermal determinations of solid phase changes were made with the same apparatus, except that a bare thermocouple was fastened in a hole drilled into the center of the specimen. Specimens weighing 175 grams were heated and cooled at the rate of 3°C. per minute.

A second set of alloys was examined for thermal transitions in the solid state by means of a modified Rosenhain furnace. This procedure differed from the previous one in that the specimens weighed approximately 8 grams and were heated under a partial vacuum to eliminate oxidation. The samples were heated and cooled at the rate of 5° to 15°C. per minute.

⁸ Wood and Cork: *Pyrometry*, 167. McGraw-Hill Book Co. New York, 1927.

The specimens were homogenized by the annealing procedure described above, prior to the thermal analysis.

Polarized Light Examination

While microscopic examination under ordinary illumination was satisfactory in most cases, there was one phase, the delta prime constituent, which could not be distinguished by it. By using polarized light this phase could be identified.

By examining a polished metal surface under polarized light an isometric metal can be determined from one that is anisometric. For making these determinations a petrographic microscope equipped with two nicol prisms, one in front of the vertical illuminator and the other above it, was used. The unetched polished specimen was mounted on the stage of the microscope and an area selected under polarized light. The analyzing nicol was then slipped into the position of crossed nicols. If the metal or metal constituent was isometric it appeared dark and no change occurred on rotating the stage 360°. If an anisometric phase occurred, individual light and dark crystals were observed. On rotating the stage 90°, the light crystals turned dark and the dark crystals turned light. A 360° rotation caused two complete extinctions of the light crystals.

When plane polarized light is reflected from the polished surface of an isometric substance, its plane of vibration is not changed. Thus the reflected light will be extinguished when the analyzing prism is put in the position of crossed nicols.

With anisometric materials, however, the plane of vibration of the reflected light is rotated so that it has a component in the vibration direction of the analyzer and some light passes through. When the specimen is rotated under crossed nicols, the only positions in which the light is completely extinguished are when the principal directions of vibrations of the reflected light coincide with the vibration direction of the light from the polarizer.

According to Farnham⁹ some metals and minerals will extinguish two times per revolution and others will extinguish four times. Antimony and stibnite, Sb_2S_3 , are typical examples, respectively. In 1930 Heindlhofer and Bain¹⁰ found that martensite gave four extinctions per revolution.

X-ray Measurements

Certain alloys were selected for analysis by means of X-rays in order to determine the nature of the phases present and also to measure their lattice parameters. The Debye-Scherrer or Hull powder method was employed, utilizing annealed filings.

⁹ Farnham; *Determination of the Opaque Minerals*. McGraw Hill Book Co. New York, 1931.

¹⁰ Heindlhofer and Bain: *Trans. Amer. Soc. Steel Treat.* (1930) **18**, 70-104.

THE COPPER-TIN SYSTEM

After considering the previous investigations of the copper-tin system, it can be seen that the results are diverse and that no two diagrams are exactly alike. Since the present study of the ternary system copper-nickel-tin was to be considered on the basis of quasibinary copper-tin systems containing constant amounts of nickel, it was necessary first to establish a copper-tin system around which the remainder of the work could be coördinated. Certain alloys were made and quenched at temperatures in the vicinity of some of the questionable points of the system; namely, the alpha-phase boundary, the gamma, gamma + beta, gamma + delta and delta fields.

The results obtained on the location of the alpha-phase boundary were in agreement with the Stockdale¹¹ diagram (Fig. 2). A specimen containing 15.5 per cent tin quenched at 590° C. contained only the alpha phase,

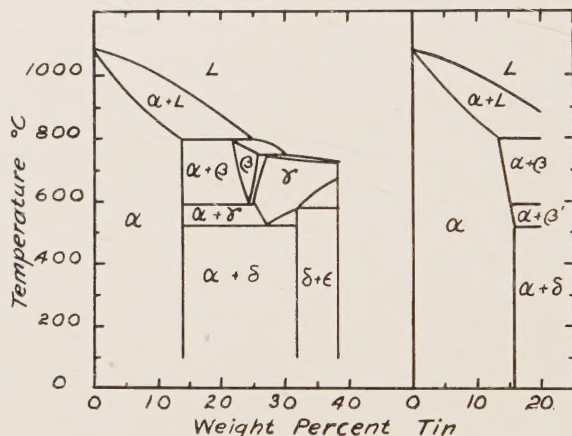


FIG. 1.

FIG. 2.

FIG. 1.—COPPER-TIN SYSTEM BY BAUER AND VOLLENBRUCK.

FIG. 2.—ALPHA-PHASE BOUNDARY OF THE COPPER-TIN SYSTEM BY STOCKDALE.

while one containing 16 per cent tin consisted of alpha with a small amount of beta. On cooling the 16 per cent tin alloy to 500° C., all the beta dissolved in the alpha. Apparently there was an increase in solubility of tin in the alpha phase on cooling to the lower temperature. No doubt the increase in solubility stops at 520° C., the temperature of the beta prime to alpha + delta change, as indicated by Stockdale. This same alloy showed no change in appearance at 300° C. and room temperature. This would show that there is not a decrease in solubility on cooling below 500° C. A 17 per cent tin alloy contained alpha + beta at 590° C. and alpha + eutectoid (alpha + delta) at room temperature.

¹¹ Stockdale: *Jnl. Inst. Metals* (1925) **34**, 111.

The Bauer and Vollenbruck¹² diagram (Fig. 1) indicates a constant solubility of 13.9 per cent tin from 798° C. to room temperature, while the Stockdale and Carson¹³ diagrams (Figs. 2 and 3) show an increase from about 13.3 to 16 per cent tin between 800° and 520° C. Stockdale indicates a constant alpha solubility from 520° to 25° C. and Carson a decrease from 16 to 15 per cent tin. The present work confirms Stockdale's diagram.

The alloy containing 27 per cent tin gave structures at various temperatures that are in agreement with the Bauer and Vollenbruck and Matsuda¹⁴ diagrams. The alloys quenched at 725° and 572° C. were homogeneous. The entire specimens were made up of large polygonal crystals, which were dark brown on etching with acid ferric chloride. The Carson diagram would require that the alloy quenched at 725° C. be beta + gamma. On cooling to 500° C. the eutectoid (alpha + delta) with a trace of excess alpha was obtained (Fig. 4). No further change occurred on cooling to room temperature.

On quenching the 31.8 per cent tin alloy at 725° C. the gamma phase was obtained (Fig. 5). A trace of a second constituent, delta, can be seen at the grain boundaries. The gamma has a spotted appearance, which would indicate that it was on the verge of breaking down. Apparently the high tin gamma constituent is unstable and very hard to retain even under drastic quenching conditions. Carson observed the same phenomena in the alloys occurring in his gamma field.

At 572° C. this same alloy contained gamma and delta phases (Fig. 6). The delta constituent formed in the grains and at the grain boundaries of the gamma phase. The gamma still had the spotted appearance. Both the Raper¹⁵ and Bauer and Vollenbruck diagrams require that at 572° C. an alloy of this composition be 100 per cent delta. Carson found, however, that gamma and delta existed at this point in about the same proportions as shown in Fig. 6. The first two diagrams indicate that delta is a compound existing below 580° C., while Carson shows it to be a solid solution existing over the range 32 to 33 per cent tin at room tem-

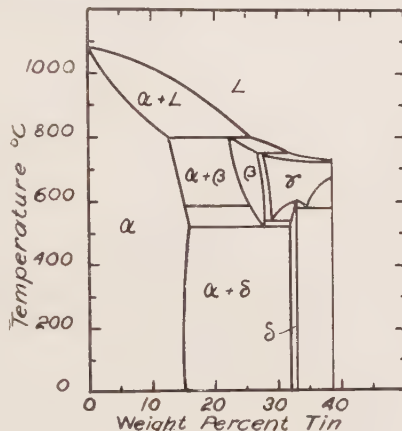


FIG. 3.—COPPER-TIN SYSTEM BY CARSON.

¹² Bauer and Vollenbruck: *Ztsch. f. Metallkunde* (1923) **15**, 119-125, 191-195.

¹³ Carson: *Canadian Min. & Met. Bull.* (Jan., 1929).

¹⁴ Matsuda: *Sci. Repts. Tohoku Imp. Univ.* (1928) **17**, 144.

¹⁵ Raper: *Jnl. Inst. Metals* (1927) **38**, 217.

perature after forming directly from gamma containing 33 per cent tin at 610° C. This would allow for a wider gamma + delta field.

At room temperature the 31.8 per cent tin alloy contained delta and a small amount of the alpha + delta eutectoid (Fig. 7). This further confirmed Carson's work that delta is not the compound Cu_4Sn , which

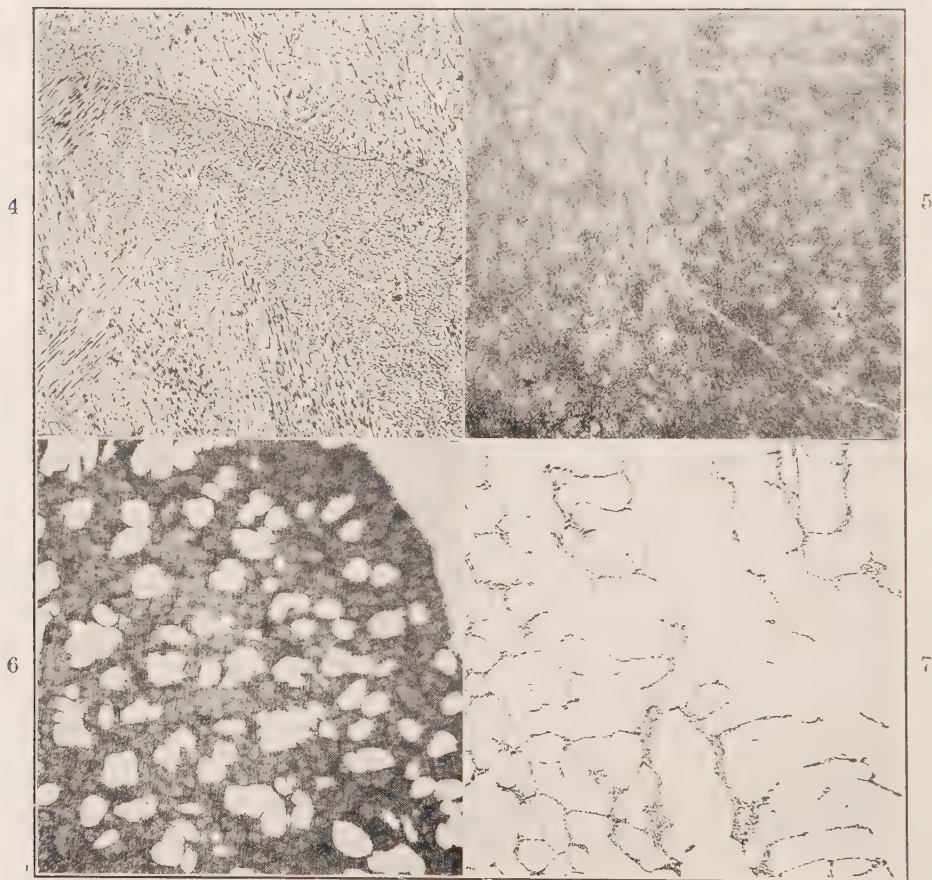


FIG. 4.—TIN, 27; COPPER, 73 PER CENT. QUENCHED AT 500° C. EUTECTOID (ALPHA + DELTA).

FIG. 5.—TIN, 31.8; COPPER, 68.2 PER CENT. QUENCHED AT 725° C. GAMMA.

FIG. 6.—TIN, 31.8; COPPER, 68.2 PER CENT. QUENCHED AT 575° C. GAMMA + DELTA.

FIG. 7.—TIN, 31.8; COPPER, 68.2 PER CENT. COOLED TO ROOM TEMPERATURE. EUTECTOID (ALPHA + DELTA) + DELTA.

ALL $\times 100$. ALL ETCHED WITH ACID FERRIC CHLORIDE.

contains 31.8 per cent tin. The results of work on the ternary system also indicate that delta is a solid solution.

After considering the results described above, it can be seen that while various parts of the different diagrams agree with them, no one diagram

does. This would suggest the putting together of parts of the diagrams to make a copper-tin diagram which agrees entirely with the present results on that system and also the ternary system. With this in mind the diagram shown in Fig. 8 was constructed. The alpha solubility from 0 to 16 per cent tin was taken from Stockdale's diagram. The solid phase changes from 16 to about 31.7 per cent tin were taken from the Bauer and Vollenbruck diagram. This part of the diagram indicates that the beta in alloys from 15.5 to 25 per cent tin changes to alpha + gamma at 590° C. While the results obtained on just the one alloy containing 27 per cent tin are by no means sufficient to establish this region, the results from the ternary alloys indicate that this diagram is more closely

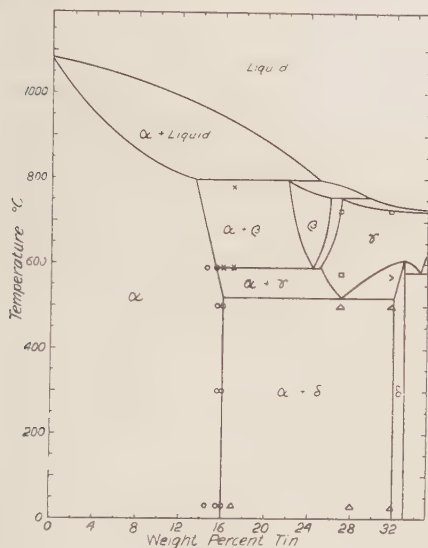


FIG. 8.

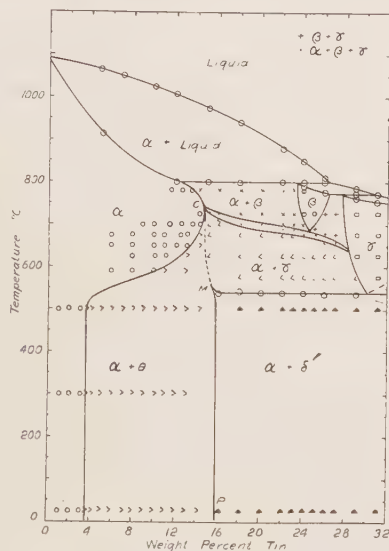


FIG. 9.

FIG. 8.—COPPER-TIN SYSTEM DERIVED FROM DIAGRAMS IN FIGS. 1, 2 AND 3. Points are shown which have been checked by the present authors.

FIG. 9.—THE 2 PER CENT NICKEL COPPER-TIN SYSTEM.

related to the ternary system than either the Raper or Carson diagrams. Above 31.7 per cent tin the Carson diagram was used.

In the following discussion of the ternary alloys, any reference to the copper-tin system refers to this constructed diagram, Fig. 8.

THE TWO PER CENT NICKEL COPPER-TIN SYSTEM

The 2 per cent nickel copper-tin system was investigated quite extensively because this amount of nickel was sufficient to produce decided changes in the microstructure and was small enough to be representative of the effects produced by the addition of small amounts of nickel to the commercial copper-tin bronzes. The equilibrium diagram of this system is shown in Fig. 9.

Liquidus and Solidus.—The liquidus and solidus temperatures that were determined are recorded in Table 3. In the diagram shown in Fig. 9, the liquidus has been extended to 1090° C. at 0 tin which was taken from the copper-nickel diagram by Guertler and Tammann.¹⁶ The present data connect very well with that temperature.

TABLE 3.—*Liquidus and Solidus Temperatures*

Ni, Per Cent	Sn, Per Cent	Solidus	Liquidus	Peritectic
2	5	913	1065	
2	7		1047	
2	10	799	1021.7	
2	12	797.5	1001.5	
2	15	798.8	971.5	
2	18	797.3	934	
2	22	800	877	
2	24	789	848	801
2	26	774	809	798
2	29	764	782.5	772.5
2	31	756.5	772.5	764.8
3	6	901	1066	
3	9	796.5	1032	
3	12.5	796.	1003.5	
3	14.5	799.5	982	
3	18	799	939.5	Solid-solid trans.
5	7	841	1067.5	801.2
5	12	818.5	1022.5	799.8
5	15	812	990	
5	18	810.5	955	
10	7	899	1096	
10	10	875	1072.5	
10	15	858	1021	
10	18	860.5	991.5	
20	7	973	1139	
20	9	926	1132.5	
20	15	936	1072.5	
20	18	936	1038.5	

A comparison with the liquidus curves of the copper-tin systems by Stockdale¹⁷ and Bauer and Vollenbruck¹⁸ shows that 2 per cent nickel raised the liquidus temperature 14° C. (average) between 5 and 18 per

¹⁶ Reference of footnote 1.

¹⁷ Reference of footnote 11.

¹⁸ Reference of footnote 12.

cent tin. Between 18 and 26 per cent tin the increase was a little higher, averaging 21°C .

The solidus horizontal extending from 12 to beyond 26 per cent tin was found to be at 799°C . Apparently the nickel has had no effect on this transition, for Stockdale as well as Bauer and Vollenbruck gave 799° and 798°C . respectively as the temperature of the solidus horizontal in the copper-tin system. A comparison of the copper-tin and 2 per cent nickel quasibinary systems shows that 2 per cent nickel has increased the tin contents of the beta, gamma and liquid phases that are in equilibrium with one another at corresponding temperatures.

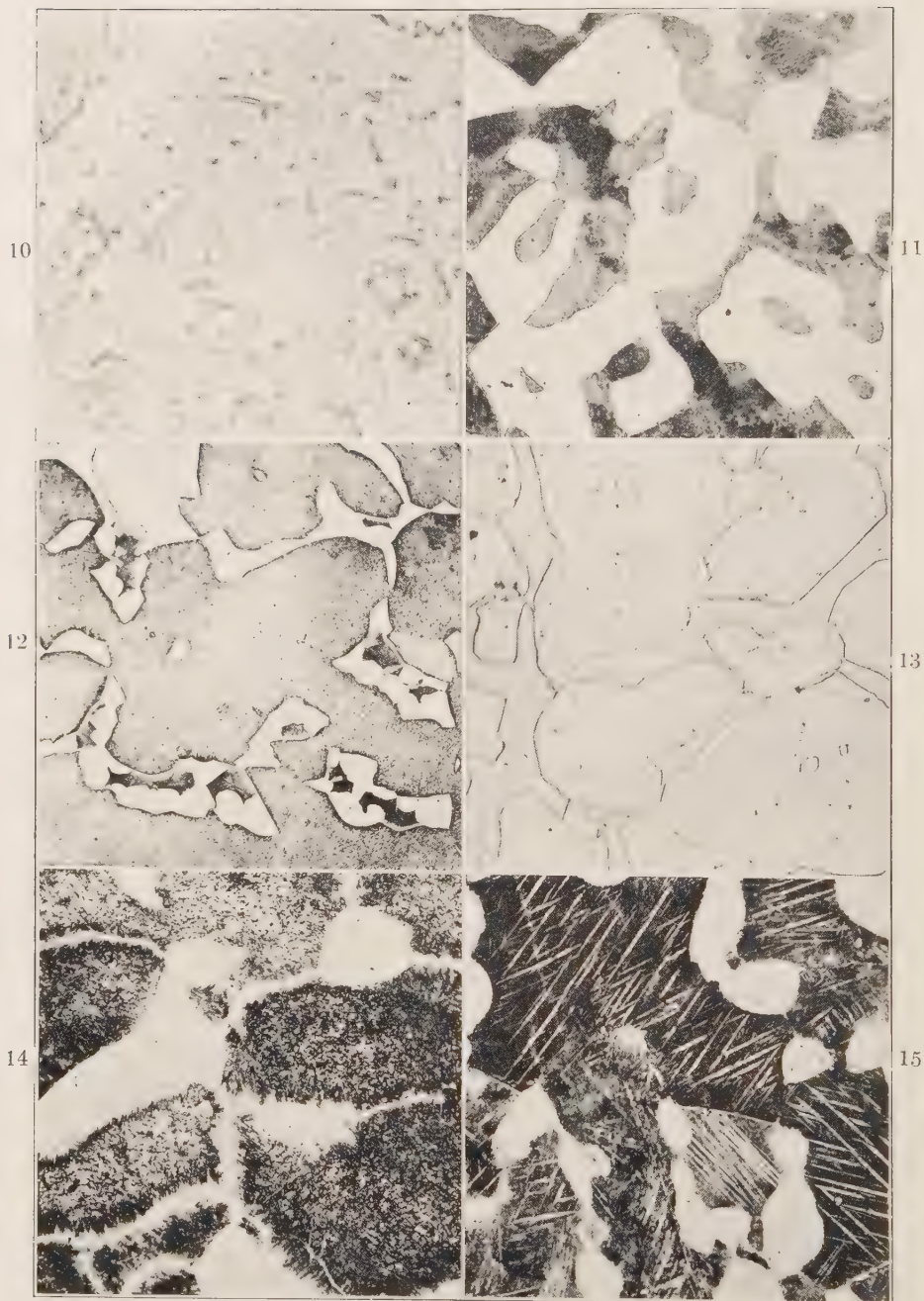
Alpha-phase Boundary.—The increase in alpha solubility, as shown in Fig. 9, on cooling from 799° to 750°C . must be associated with a solute which is related to the beta phase. On cooling to between 750° and 700°C . the beta began to change to gamma, which in itself was an unstable constituent. As the gamma formed, the atoms of the alpha must likewise have changed their arrangement to some other form. When this occurred, insoluble nuclei were formed and an excess phase was precipitated if the tin content exceeded that of the alpha boundary. The precipitated phase has been designated as theta. The reasons for considering this a new phase will be explained later. The addition of 2 per cent nickel caused a decrease of more than 12 per cent tin in the alpha solubility at 25°C . compared to what it is in the simple copper-tin system.

The X-ray pattern obtained for a 12 per cent tin alloy containing 2 per cent nickel that had been annealed and quenched at 780°C . was typical of a face-centered cubic structure. The lattice constant computed from the measurements was $3.680\text{ \AA}$.

An interpolation of the values reported by Weiss¹⁹ on the alpha phase of the copper-tin system for a 12 per cent tin alloy gives $3.673\text{ \AA}$. This is only $0.007\text{ \AA}$ less than the above value. This shows that the addition of 2 per cent nickel has produced very little effect on the lattice parameter of the alpha phase.

Alpha + Beta Field.—The beta constituent was not retained in a homogeneous state even under very drastic quenching conditions. There was always a narrow blue band around it due to a partial decomposition. In the specimens containing small amounts of beta, the bands were more pronounced than in those containing large amounts, as can be seen by comparing Figs. 11, 14 and 15. Apparently the stability of the beta increased with the quantity present. It can also be seen that as the degree of supersaturation of the beta diminished, the tendency for the formation of the transition boundaries on quenching decreased. The alloys quenched at 780°C . contained more of the border effect than those

¹⁹ Weiss: *Proc. Roy. Soc.* (1925) **108A**, 643-654.



FIGS. 10-15.—CAPTIONS ON OPPOSITE PAGE.

quenched at 725° and 700° C. Stockdale observed this reaction rim around the beta phase in his study of the alpha + beta alloys of the copper-tin system.

Beta Field.—On comparing the beta field with that of the copper-tin system in Fig. 8, one can see that the presence of 2 per cent nickel caused a pronounced decrease in its size and a rise in the inversion point to alpha + gamma from 587° C. to 685° C.

The X-ray measurements of the beta constituent showed that the nickel addition caused an increase in the lattice parameter. A lattice constant of 2.994 Å was obtained for the 25 per cent tin alloy quenched at 725° C. Neuburger²⁰ gives the constant for a 15 atomic per cent tin (24.8 weight per cent) alloy quenched from the beta field to be 2.972 Å. Patterns typical of body-centered cubic crystals were obtained in both investigations.

Beta + Gamma Field.—There is a decided change in the shape of the beta + gamma field. Whereas in the copper-tin system it decreases in width from 1 per cent tin at 755° C. to less than 1 per cent at 587° C., in the 2 per cent nickel copper-tin system it increases in width from about 1.3 per cent tin at 773° C. to more than 3 per cent at the lower boundary. Both the upper and lower boundaries are raised in temperature.

The alloys in this area exhibited a peculiar flowerlike structure. In an alloy containing 26 per cent tin, quenched at 725° C., the gamma had separated at the edges of the beta grains in long crystals and in the beta grains in irregular sharp-cornered particles. On cooling this alloy to 675° C., the amount of the gamma increased so that it tended to form borders around the beta grains (Fig. 21). The interior particles increased in size and lost some of their sharpness and irregularity. In both cases the beta had a striated appearance.

The striations in the beta look like slip bands in that they are fine lines running in parallel directions in individual grains. These striations were probably caused by an internal strain in the beta grains. They could be due either to the quench itself or to a precipitation of the gamma

FIG. 10.—NICKEL, 2; TIN, 10; COPPER, 88 PER CENT. QUENCHED AT 300° C. ALPHA + THETA. $\times 1000$.

FIG. 11.—NICKEL, 2; TIN, 18; COPPER, 80 PER CENT. QUENCHED AT 780° C. ALPHA + BETA (BLACK). $\times 100$.

FIG. 12.—NICKEL, 2; TIN, 18; COPPER, 80. QUENCHED AT 700° C. ALPHA (GRAY) + BETA (BLACK) + GAMMA (WHITE). $\times 100$.

FIG. 13.—NICKEL, 2; TIN, 20; COPPER, 78 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + DELTA PRIME. $\times 100$.

FIG. 14.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 780° C. ALPHA + BETA (BLACK). $\times 100$.

FIG. 15.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 725° C. ALPHA + BETA (ACICULAR). $\times 100$.
Etched with acid ferric chloride.

²⁰ Neuburger: Röntgenography of the Metals and Their Alloys, 144–151. F. Enke, Stuttgart, 1929.



FIGS. 16-21.—CAPTIONS ON OPPOSITE PAGE.

phase along the crystal planes. The latter cause would seem to be the more probable.

Alpha + Beta + Gamma Field.—The beta change at 587° C. in the copper-tin system was raised to 750° C. at the high copper side and to 640° C. at the tin-rich side by the addition of 2 per cent nickel. Hoyt believed that the change at 590° C. in the copper-tin system was due to a transformation of the beta to alpha + gamma. This effect appears to have been accentuated by the presence of 2 per cent nickel, for a narrow field approximately 17° C. in width instead of a line was found to exist between 18 and 25 per cent tin. Below 18 and above 25 per cent tin the area diminished in width to 0° C. at 14.5 and 28 per cent tin respectively.

Fig. 12 shows the three phases obtained by quenching an 18 per cent tin alloy at 700° C. On comparing this with Fig. 11, it can be seen that the beta has almost completely changed to gamma. Fig. 19 shows the beginning of the gamma formation in the beta phase, which is partially striated. In a 24 per cent tin alloy quenched at 675° C., the beta + gamma phases had the flowerlike structure of the alloys occurring in the beta + gamma field and the alpha occurred as lozenge-shaped grains (Fig. 20).

From these observations it can be seen that the beta change occurring in this range is not a transformation to a eutectoidal structure of alpha + gamma, but merely a change to these two phases by a two-stepped transformation. First, the beta changes to gamma, which has a lower solubility for copper than the beta. Second, owing to this decrease in copper solubility in the gamma phase, there is a migration of the atoms and the alpha phase, which is copper rich, is precipitated. The alpha is always precipitated at the grain boundaries of the gamma and never between beta and gamma grains, where the differences in composition between the two phases tend to adjust themselves.

The beta change at 587° C. in the copper-tin system may well be the same kind of transformation. In the absence of nickel, the change occurs at a more rapid rate.

Gamma Field.—The 29 per cent tin alloys that were quenched at temperatures within the gamma field were homogeneous. The 31 per cent tin alloys, however, were of an unstable nature, as those that were

FIG. 16.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 675° C. ALPHA + GAMMA (DARK). $\times 100$.

FIG. 17.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. QUENCHED AT 575° C. ALPHA + GAMMA (DARK). $\times 100$.

FIG. 18.—NICKEL, 2; TIN, 22; COPPER, 76 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). $\times 100$.

FIG. 19.—NICKEL, 2; TIN, 23; COPPER, 75 PER CENT. QUENCHED AT 688° C. ALPHA (WHITE) + BETA (DARK) + GAMMA (IRREGULAR SHAPED). $\times 100$.

FIG. 20.—NICKEL, 2; TIN, 24; COPPER, 74 PER CENT. QUENCHED AT 675° C. ALPHA + BETA + GAMMA. $\times 100$.

FIG. 21.—NICKEL, 2; TIN, 26; COPPER, 72 PER CENT. QUENCHED AT 675° C. GAMMA + BETA (STRIATED). $\times 100$.

Etched with acid ferric chloride.

quenched above 625°C . contained a small quantity of precipitated delta prime. The alloy quenched at 575°C . was homogeneous. These same phenomena were observed by Matsuda²¹ in his study of the copper-tin alloys.

Several attempts were made to obtain X-ray diffraction patterns of 31 per cent tin alloys quenched at 725°C . Very poor patterns were obtained and sometimes no definite lines were found after 12 hr. exposure. The unstable condition of the gamma constituent caused diffuse lines. This same phenomenon was observed by Carson in his work on the gamma phase of the copper-tin system.

Alpha + Gamma Field.—One of the most striking characteristics of the alloys occurring in this field was the variation in appearance of the gamma phase. At the high temperatures near the alpha + beta + gamma boundary the gamma phase had a light blue color after etching with acid ferric chloride, while at temperatures near the lower boundary it was dark blue. This is illustrated in Figs. 16 and 17. The same was true with the variation of the tin content. As the tin increased, the gamma changed from a light blue color to a dark blue-brown color.

The lower boundary of the field was determined by thermal examinations of seven alloys varying in tin content from 16 to 29 per cent tin. The thermal changes varied within the limits of 537° to 542°C ., indicating a gamma eutectoid inversion at 539°C .

Alpha + Theta Field.—The theta constituent was clear and had a light blue color on etching with acid ferric chloride. It had a nodular and needlelike form, as is shown in Fig. 10 (a 10 per cent tin alloy quenched at 300°C .). While most of it occurred as a precipitated phase in the alpha, some of it is also located at the grain boundaries.

The theta constituent was considered to be different from the gamma phase, for the following reasons. A thermal examination of a homogenized 14.2 per cent tin alloy did not indicate any change between 500° and 650°C . This would indicate that the same phase was present from temperatures just below the alpha-phase boundary to below 500°C . The addition of 2 per cent nickel raised the temperature of the gamma inversion to

FIG. 22.—NICKEL, 2; TIN, 27; COPPER, 71 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). $\times 100$.

FIG. 23.—NICKEL, 5; TIN, 29; COPPER, 66 PER CENT. COOLED TO ROOM TEMPERATURE. ALPHA + DELTA PRIME (WHITE). $\times 100$.

FIG. 24.—NICKEL, 2; TIN, 20; COPPER, 78 PER CENT. COOLED SLOWLY TO ROOM TEMPERATURE. REHEATED AND COOLED THROUGH 539°C . AT A RATE OF 10°C . PER MINUTE. ALPHA + EUTECTOID (ALPHA + DELTA PRIME). $\times 1000$.

FIG. 25.—NICKEL, 5; TIN, 13; COPPER, 82 PER CENT. COOLED TO ROOM TEMPERATURE (COOLED FROM 700° TO 500°C . IN 10 HR.). ALPHA + THETA. $\times 100$.

FIG. 26.—NICKEL, 20; TIN, 9; COPPER, 71 PER CENT. COOLED TO ROOM TEMPERATURE (COOLED FROM 725° TO 500°C . IN 94 HR.). ALPHA + THETA. $\times 1000$. Etched with acid ferric chloride.

²¹ Reference of footnote 14.



FIGS. 22-26.—CAPTIONS ON OPPOSITE PAGE.

539° C. This is 19° C. higher than in the copper-tin system. It is not very probable that the nickel would lower the temperature domain of gamma in one case and raise it in another; therefore, the excess constituent in this field has been designated as a new phase, theta.

On considering the instability of the gamma phase it seemed very likely that the gamma in low-tin alloys changed to theta over a range of temperature; so a sloping line *CM* was drawn to indicate the boundary between the alpha + theta and alpha + gamma fields. This boundary intersects the alpha boundary at a temperature slightly lower than do the boundaries of the alpha + beta + gamma field.

The microstructure of these alloys, together with those of the higher nickel alloys, discussed later, indicate that the theta phase might be either the compound Ni_4Sn or Ni_3Sn of the nickel-tin system reported by Voss,²² or what is more probable, one of these compounds containing copper in solid solution.

Alpha + Delta Prime Field.—The alpha + delta prime field was located between 539° C. and room temperature for alloys containing from 16 to beyond 31 per cent tin. The boundary on the high tin side was not determined. The alloys containing from 16 to 20 per cent tin that were quenched at 500° C. and also those cooled to room temperature contained alpha plus a clear delta prime constituent (Fig. 13).

The alloys from 22 to 29 per cent tin consisted of alpha + eutectoid (alpha + delta prime) (Figs. 18 and 22). These photomicrographs show that the amount of alpha precipitate in the eutectoid increased with the tin content. The 22 and 23 per cent tin alloys had very little alpha in the delta prime and most of it was in the center of the delta prime grains, while the 27 and 29 per cent tin alloys had considerable quantities of alpha in the delta prime phase.

The existence of the new phase delta prime was established by the following observations:

1. On etching with acid ferric chloride, delta prime was white, while the gamma constituent in alloys from 18 to 29 per cent tin varied in color from a pale blue to a dark blue-brown color respectively.

2. The thermal examinations of the alloys from 16 to 29 per cent tin indicated a thermal change at 539° C. which was in agreement with a phase transformation.

3. The difference in the behavior of the delta prime phase from all other phases when examined under polarized light. A large number of alloys were examined under polarized light so that the behavior of every phase in the diagram could be determined. The results show that in every case the delta prime phase reversed colors when rotated in the polarized light. On rotating 360°, it was white twice and dark twice. It did not reverse as a solid mass but as individual crystals. First one would

²² Reference of footnote 3.

turn dark and then another, depending upon the orientation of the crystals. All of the other phases in this system did not reverse colors when rotated, but remained dark. This indicated that delta prime does not have a cubic structure and that all the other phases do have.

Delta prime, although having the same color and appearance when examined under the ordinary microscopic procedure as the delta of the copper-tin system, differed from it under polarized light. Delta did not reverse colors. According to Westgren and Phragmen²³ delta has a face-centered cubic lattice with 416 atoms to the unit cell. This is without doubt a very peculiar type of structure. A small amount of nickel was sufficient to change this cubic structure to perhaps a tetragonal or a hexagonal phase. This being the case, delta prime would reverse colors when viewed under polarized light.

In the same manner delta prime was distinguished from the theta phase. The line *CMP* was drawn from 14.5 per cent tin, 749° C., to 15.8 per cent tin, 25° C., because there was a definite moving to the right of the corresponding line in the 3 and 5 per cent nickel systems.

The 31 per cent tin alloy quenched at 500° C. contained delta prime + eutectoid (alpha + delta prime). When it was cooled to room temperature the amount of excess delta prime increased. The same phenomena were observed in the 1 per cent nickel alloys. Since the alpha-phase boundary did not vary from 500° to 25° C., the change must be entirely in the delta prime phase. This would indicate that delta prime was a solid solution whose solubility for copper and nickel increased on cooling below the eutectoid transformation.

After considering the structures of the alloys in this field the question arises as to why the high-tin alloys have a eutectoid structure and the low-tin alloys do not. It can be explained in the following manner:

1. The addition of nickel moves the location of the gamma eutectoid to higher percentages of tin. It is assumed that the delta prime phase boundary is moving also to higher tin percentages but not as rapidly as the eutectoid. As the distance between the eutectoid point and the delta prime phase boundary is decreased, the amount of alpha in the eutectoid is decreased.

2. On cooling below the eutectoid transformation, the solubility of copper and nickel in the delta prime is increased so that part of the alpha in any eutectoid present is absorbed by the delta prime.

3. The diffusion rates of the atoms must be greater in the delta prime phase than in the ordinary delta, so that when an alloy is cooled slowly through the eutectoid inversion the resulting phases come to a state that is nearer to equilibrium. In other words, the copper and nickel atoms migrate at a faster rate to either the already existing alpha boundaries or to coalesce with one another and form coarse alpha particles in the delta

²³ Westgren and Phragmen: *Ztsch. f. Metallkunde* (1926) **18**, 279-284.

prime than in nickel-free alloys. When the delta prime grains are small and the migration distances are short a clear delta prime will result, and when the delta prime crystals are large a coarse eutectoid will be formed. These two cases are represented by the 20 and 29 per cent tin alloys.

The fact that the rate of cooling plays an important part in the structure obtained can be seen by comparing two 20 per cent nickel alloys, Figs. 13 and 24, that were cooled at two different rates. The first structure was obtained by the annealing and very slow cooling treatment used in determining the equilibrium diagram and the second by reheating and cooling this annealed alloy through 539° C. at the rate of 10° C. per minute. The delta prime of the annealed and very slowly cooled alloy is homogeneous while the other has a eutectoidal structure.

THE ONE PER CENT NICKEL COPPER-TIN SYSTEM

There was such a decided shift in the location of the eutectoid point, gamma to alpha + delta prime, in the 2 per cent nickel copper-tin system from that of the straight bronze that it seemed wise to locate it at some composition between the two systems. Four alloys were made containing 1 per cent nickel with the tin varying from 27 to 30 per cent and were quenched at temperatures varying from 725° to 500° C. A set of alloys also was slowly cooled to room temperature.

The results obtained from the heat treatments of the four alloys are exactly what one would expect to find on assuming a gradual change from the copper-tin system to the 2 per cent nickel quasibinary system. The eutectoid point was located at 28.5 per cent tin.

THE THREE AND FIVE PER CENT NICKEL COPPER-TIN SYSTEMS

The 3 and 5 per cent nickel copper-tin systems were not developed as extensively as the 2 per cent series has been. The alpha-phase boundary together with the solidus and liquidus above that field were determined. Five additional alloys in each system exceeding the alpha limit and containing as high as 29 per cent tin were quenched at the same standard temperature intervals as were the 2 per cent nickel alloys. While the latter observations did not give enough information to fully establish the systems, they do agree with the results obtained for the previous systems and show the general trend of the phase changes caused by further nickel additions. These systems are shown in Figs. 27 and 28.

Liquidus and Solidus.—The temperature of the liquidus in both the 3 and 5 per cent nickel systems was raised 7° C. for each per cent of nickel compared to the copper-tin system.

The solidus horizontal in the 3 per cent nickel system above the alpha + beta field was located at 799° C., which is the same as the 2 per cent nickel system. With 5 per cent nickel it was at 812° C.

Alpha-phase Boundary.—The solubility of tin in the alpha phase in both the 3 and 5 per cent nickel systems decreased from 12.5 to less than

1.5 per cent tin between 780° and 500° C. The shape of the boundary in the 3 per cent nickel quasibinary is very similar to that of the 2 per cent nickel system. The boundary of the 5 per cent system differs from the other two in that the tin solubility decreased more rapidly between 780° and 700° C. No further change in solubility occurred on cooling below 500° C. in either case.

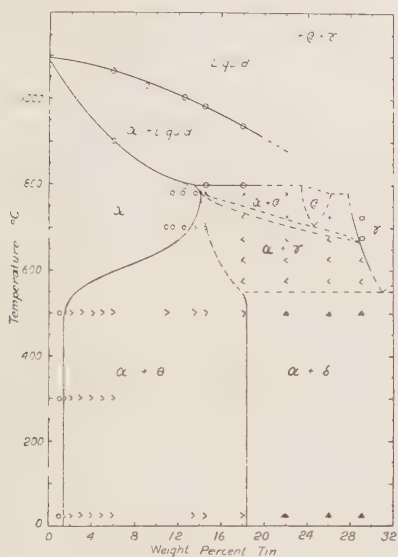


FIG. 27.

FIG. 27.—THE 3 PER CENT NICKEL COPPER-TIN SYSTEM.

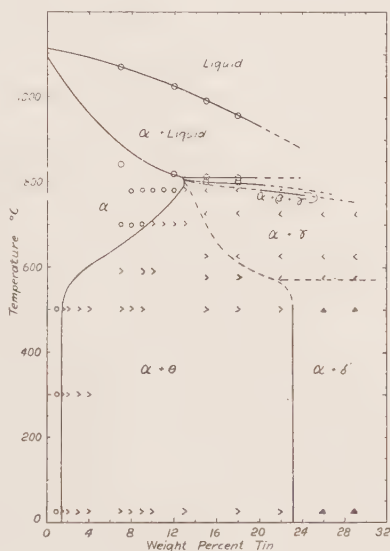


FIG. 28.

FIG. 28.—THE 5 PER CENT NICKEL COPPER-TIN SYSTEM.

Solid Phase Changes Outside Alpha Boundary.—The phases present in the alloys that exceed the alpha boundary show that further nickel additions have a progressive effect on the location of the boundaries of the various fields. As in the 2 per cent nickel system, the addition of 3 and 5 per cent nickel raised the temperature domain and restricted the size of all the areas containing the beta phase. In the 5 per cent nickel system, the alpha + beta + gamma field was within 11° C. of the peritectic horizontal. The rate at which the alpha + beta field has been diminished in size and the raising of the triplex field would indicate that the beta constituent would finally vanish on further nickel additions.

The boundary between the alpha + theta and alpha + delta prime fields was raised to higher percentages of tin in both systems. In the 3 per cent nickel quasibinary the alpha + delta prime alloys containing below 26 per cent tin had a clear delta prime phase, while those above had a eutectoid structure. All of the 5 per cent nickel alpha + delta prime alloys had a clear delta prime phase (Fig. 23). As the nickel was increased

from 3 to 5 per cent in the 29 per cent tin alloys the amount of excess alpha increased, indicating that the delta prime phase boundary has been raised to a higher tin content as the nickel increased.

THE TEN AND TWENTY PER CENT NICKEL COPPER-TIN SYSTEMS

The study of the 10 and 20 per cent nickel systems has been limited to the determination of the alpha-phase boundary.

The 10 Per Cent Nickel Copper-tin System.—The diagram of this system is shown in Fig. 29. The average increase in the liquidus temperature for each per cent of nickel was 6.8°C . The peritectic horizontal was located at 859°C ., which is 61°C . higher than in the simple copper-tin system.

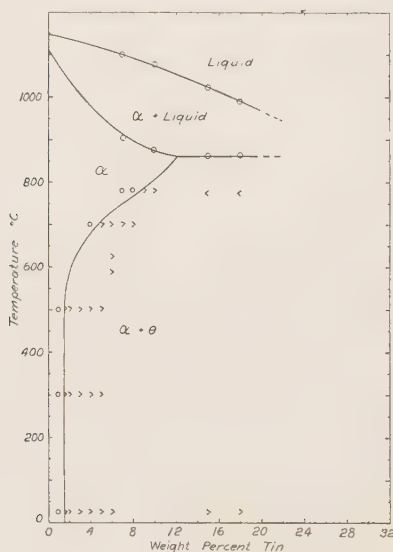


FIG. 29.

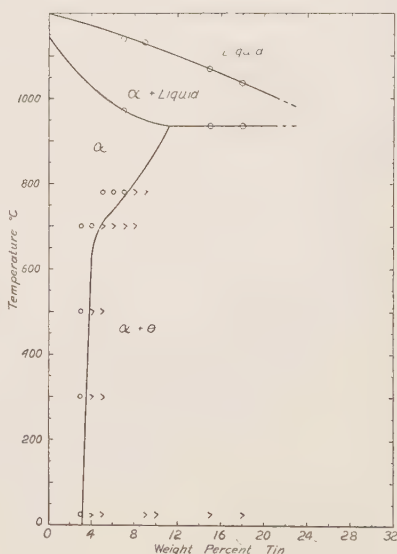


FIG. 30.

FIG. 29.—THE 10 PER CENT NICKEL COPPER-TIN SYSTEM.

FIG. 30.—THE 20 PER CENT NICKEL COPPER-TIN SYSTEM.

The alpha boundary decreased from about 8.7 per cent tin at 780°C . to slightly less than 1.5 per cent at 500°C ., and room temperature. The alpha + theta phases were present in alloys exceeding the solubility limit.

The 20 Per Cent Nickel Copper-tin System.—The diagram of this system is shown in Fig. 30. The average increase in the liquidus temperature above that of the copper-tin system was 5.7°C . for each per cent of nickel. The peritectic horizontal was located at 936°C ., an increase of 138°C .

There was not as great a decrease in the solubility of tin in the alpha with decreasing temperature as in the other systems. This alpha solubility also differed from the others in that it decreased on cooling from

500° to 25° C. The boundary varied from about 7.2 to 3.1 per cent tin between 780° and 25° C.

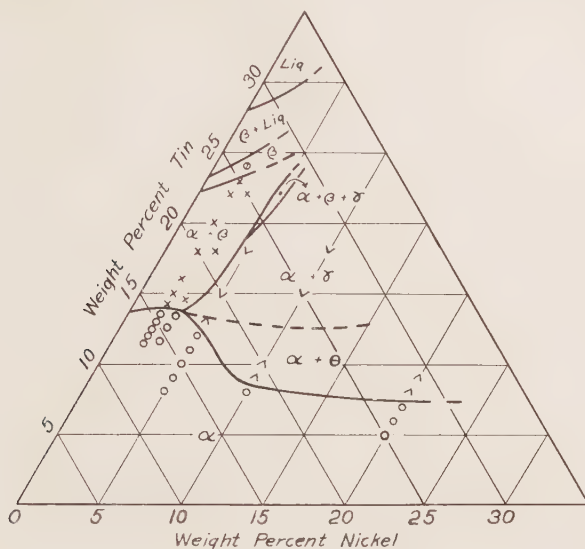


FIG. 31.—THE 780° C. ISOTHERM.

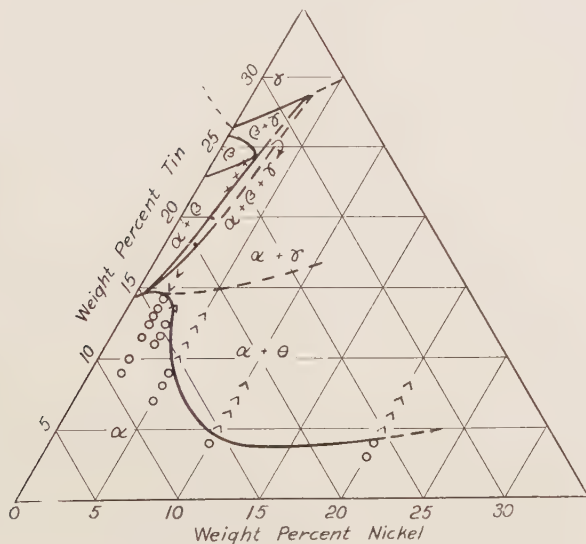


FIG. 32.—THE 700° C. ISOTHERM.

MICROSTRUCTURE OF ALLOYS IN THE ALPHA + THETA FIELD

Upthegrove, Wilson and Rhines²⁴ found that slowly cooled alloys containing 15 per cent tin and 3 to 10 per cent nickel consisted of dark-

²⁴ Reference of footnote 5.

etching alpha containing particles of the light theta phase, similar to Fig. 25. Price, Grant and Phillips²⁵ also found that alloys in the alpha + theta field had a dark color after etching.

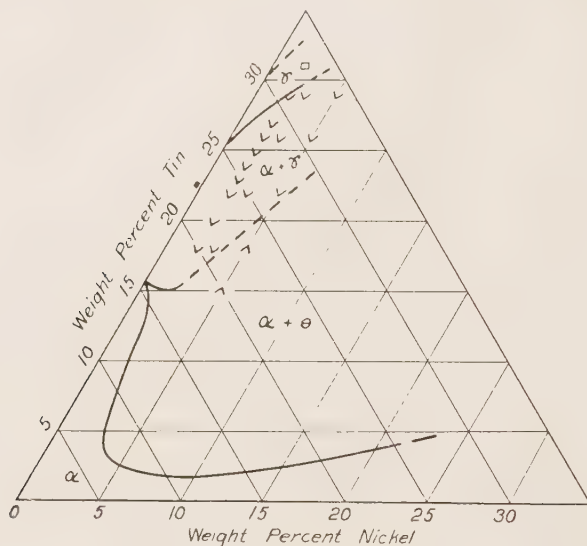


FIG. 33.—THE 575° C. ISOTHERM.

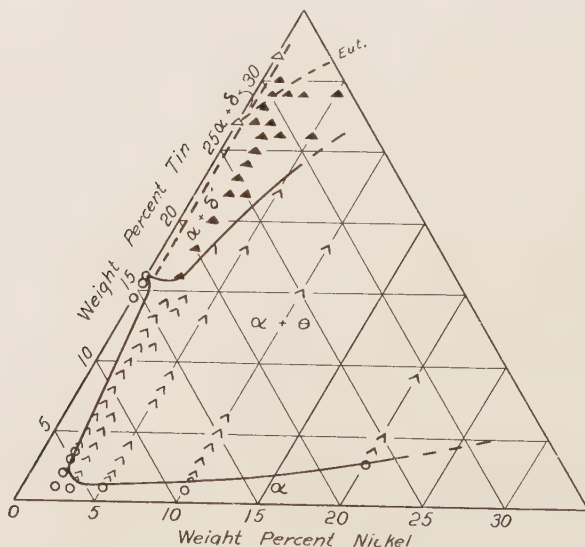


FIG. 34.—THE 500°, 300° AND 25° C. ISOTHERM.

The observations of the present authors show that the microstructure of alloys in this field depends upon the rate of cooling through the temper-

²⁵ Reference of footnote 4.

ature range in which the solubility of tin decreases in the alpha phase. When an alloy is cooled fairly rapidly through this temperature range, the theta constituent is precipitated in a very finely divided state in the alpha. After etching, this mixture has a dark appearance as shown in Fig. 25, which is a photomicrograph of a 5 per cent nickel and 13 per cent tin alloy cooled from 700° to 500° C. in 10 hr. When these alloys are cooled at a much slower rate, the theta phase coalesces into large grains and the alpha matrix is clear after etching. Fig. 26 shows the clear alpha matrix and large theta particles in a 20 per cent nickel, 9 per cent tin alloy which was cooled from 725° to 500° C. in 94 hours.

SUMMARY

The results of the investigation can be summarized clearly by considering several isothermal diagrams of the ternary system. Figs. 31 to 34 give the isotherms at 780°, 700°, 575° and 500°, 300°, 25° C. respectively.

A survey of the isotherms shows that as the nickel is increased the boundaries of the beta and gamma fields move to higher tin contents. As the temperature is lowered all the areas containing the beta phase contract to lower nickel contents. The alpha + gamma field likewise diminishes in size at the lower temperatures.

The gamma and alpha + gamma fields present at 575° C. are replaced by the alpha + delta and alpha + delta prime areas in the 500° C. isotherm (Fig. 34). The dotted line extending from 16 to 32 per cent tin at approximately 0.5 per cent nickel indicates that a definite amount of nickel probably is required to produce alpha + delta prime. The broken line across the top of the diagram indicates the shift in the gamma eutectoid inversion to alpha + delta prime to higher percentages of tin as the nickel is increased in amount.

The solubility of tin in the alpha phase in all the isotherms starts to decrease at the nickel content at which the alpha comes in equilibrium with the theta phase, which varies between about 0.5 and 3.5 per cent nickel.

CONCLUSIONS

After considering the various quasibinary systems and the ternary isotherms, the following conclusions were reached concerning the copper-rich alloys of the copper-nickel-tin system:

1. The solubility of tin in the alpha phase of the copper-tin system increases between 590° and 500° C. and then remains constant to room temperature.
2. The transformation in the copper-tin system between 15.5 and 25 per cent tin at 590° C., which was observed by Hoyt, Stockdale and others, is due to a change of the beta phase to alpha + gamma.
3. The liquidus of the bronzes containing up to 18 per cent tin is increased 7° C. for each per cent of nickel added up to 5 per cent. Above

that amount of nickel the gradient diminishes to 5.7° C. at 20 per cent nickel.

4. Alloys containing up to 10 per cent nickel exhibit a greater temperature difference between the liquidus and the solidus horizontal above the $\alpha + \beta$ field than do the simple copper-tin alloys.

5. The addition of nickel to copper-tin alloys causes the solubility of tin in the α phase to increase on cooling below the solidus when the α is in equilibrium with the β phase. The solubility of tin in the α decreases on cooling below the temperature at which β changes to $\alpha + \gamma$. A new phase, θ , is then precipitated.

6. The α solubility at 500° , 300° and 25° C. decreases from 16 per cent tin at 0 per cent nickel to a minimum of approximately 1.2 per cent tin at 4 per cent nickel, followed by a gradual increase to slightly over 3 per cent tin at 20 per cent nickel.

7. The lattice parameter of the α phase of an alloy containing 2 per cent nickel and 12 per cent tin quenched at 780° C. is $3.680 \text{ \AA}$. The parameter of the β phase of an alloy containing 2 per cent nickel and 25 per cent tin quenched at 725° C. is $2.994 \text{ \AA}$.

8. The addition of nickel raises the temperature of the β transformation to $\alpha + \gamma$ and causes the change to be more sluggish and to extend over a range of temperature. This transformation does not occur at constant temperature, but takes place at higher temperatures as the copper or nickel content increases.

9. The addition of nickel to the δ phase of the copper-tin system causes it to change from a cubic structure to an anisometric structure, which has been designated as δ prime. δ prime is a solid solution in which the solubility of copper and nickel increases on cooling below the eutectoid transformation; thus causing an absorption of part of the α .

10. The addition of nickel causes the γ eutectoid point to move to higher tin contents.

11. In alloys containing 2 per cent nickel and at least 16 per cent tin, the γ phase changes to $\alpha + \delta$ prime on cooling through 539° C. Whether or not the eutectoid structure of $\alpha + \delta$ prime is obtained, depends upon the rate of cooling. A rapid rate of cooling tends to give a fine eutectoid structure, while a very slow rate of cooling gives a clear δ prime phase in the low-tin alloys and a coarse eutectoid structure in the high-tin alloys. By slow cooling the α is given an opportunity to coalesce at the grain boundaries.

12. Alloys in the $\alpha + \theta$ field containing at least 5 per cent nickel when cooled to room temperature may contain either a clear or dark-etching α matrix, depending upon the rate of cooling through the temperature range in which the solubility of tin in the α phase decreases. A relatively fast rate of cooling causes the θ constituent to separate in a very fine precipitate in the α , causing a dark

appearance on etching. A very slow rate of cooling allows the theta phase to coalesce to large grains and the alpha remains light in color.

ACKNOWLEDGMENTS

The authors desire to express their appreciation to Prof. W. P. Wood and to Prof. Lars Thomassen for their cooperation and assistance in this investigation; and to Messrs. O. Leone, D. McCutcheon, and J. Lester, who aided in the experimental work.

